# Tunable Resonance Raman measurements of Suspended, Individual, SWNTs

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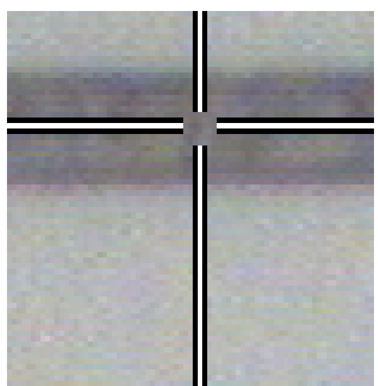
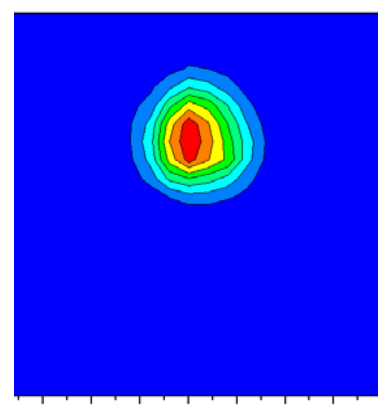





NIST-NASA workshop, Jan 2005

# Our goal of SWNT studies

- How does a tubes electronic states respond to perturbations?

Electronic model

Optical excitation resonance ($E_{ii}$):
e-h pair excitons vs
band edge resonances

“Environmental” effects,
perturbations

Heat, strain, doping, $\varepsilon$,
interfaces, schmutz…

(n,m) assignments

Identifiers like $E_{ii}$ not
fixed for given (n,m) tube

# Ensemble vs. single tube measurements

Ensembles:

- "Big picture"
- Statistically valid
- Inhomogeneous broadening
- Cannot follow how perturbation affects a tube

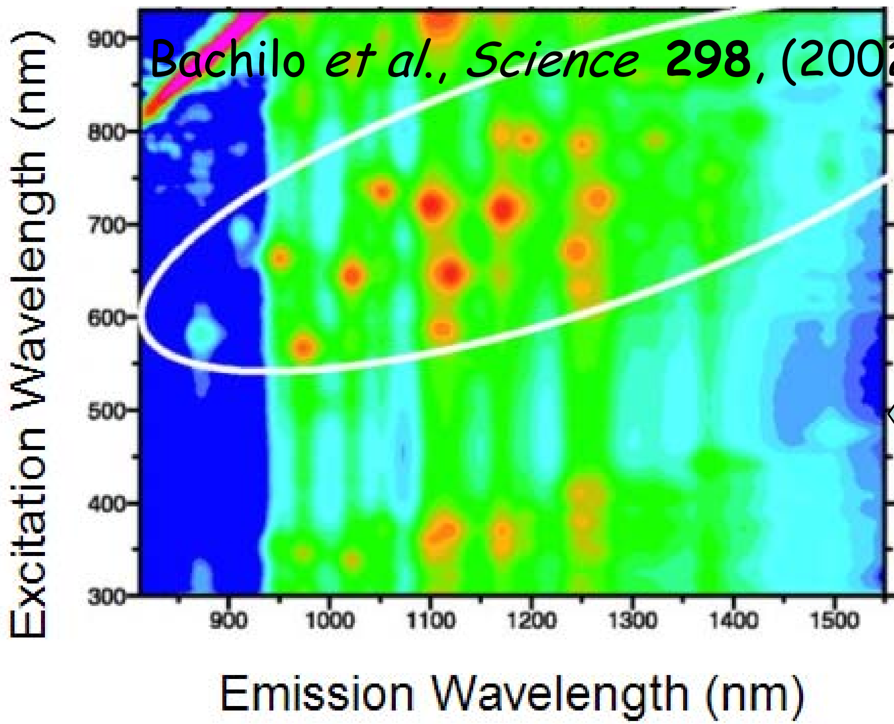
Single tube:

- Detailed information, e.g. lifetime, $E_{ii}$(strain)
- Harder to get statistics
- Harder measurements

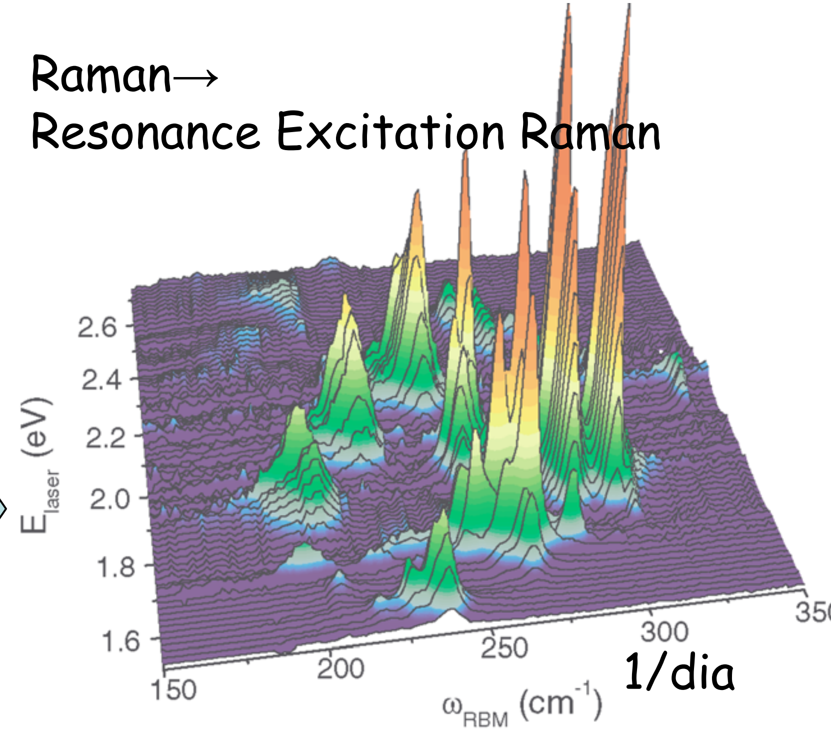
# Ensemble measurements -Adding a variable…

PL→PLE

Bachilo *et al.*, *Science* **298**, (2002)

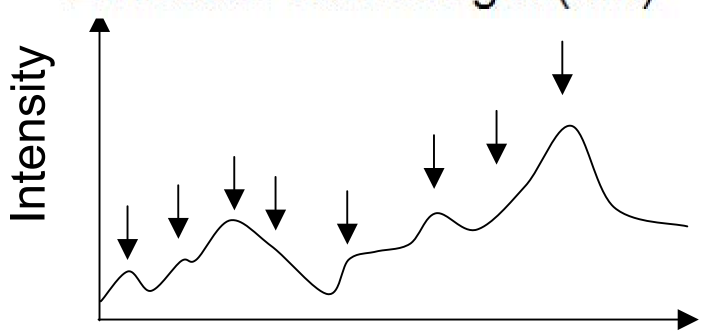



Raman→
Resonance Excitation Raman



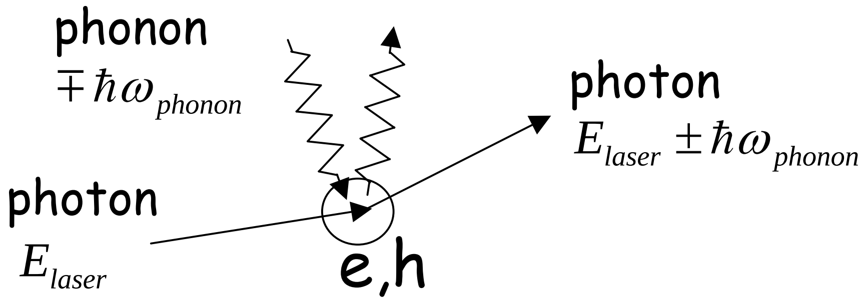

1/dia

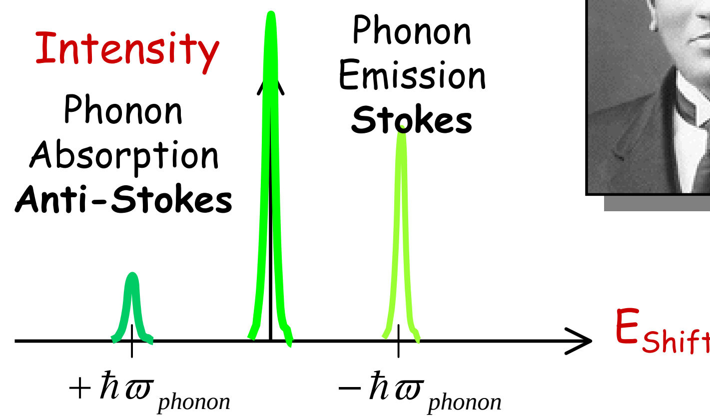
Fantini, PRL 93 (2004)

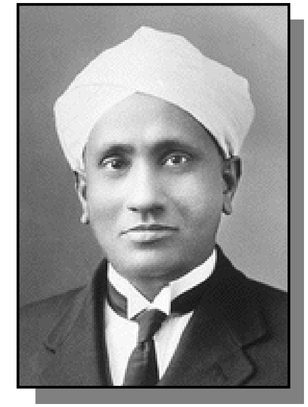



PLE → (E22, E11), only SC
Res Ex Raman → ($E_{ii}$, diameter) SC+M
→ (n,m) identification,
→ "Family pattern"

# Raman Spectroscopy



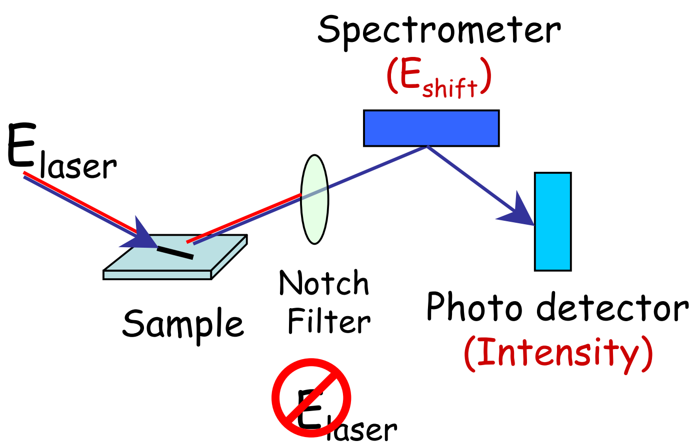



Energy and momentum conservation → Probing of optical ZC phonons (mostly)

Measures Raman Shift, i.e., quantized phonon energy:

- →Material identification
- →Elastic properties and strain
- →Temperature probe
- →…




## Resonant Raman spectroscopy

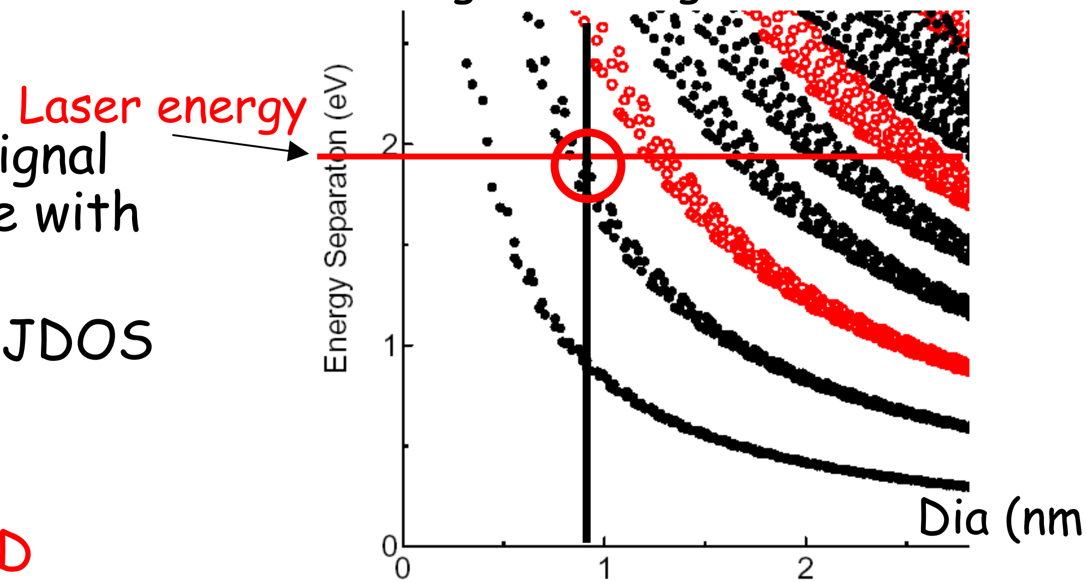
*We will add Raman Intensity measurements to also probe the electronic structure*

# Role of Raman for CNTs

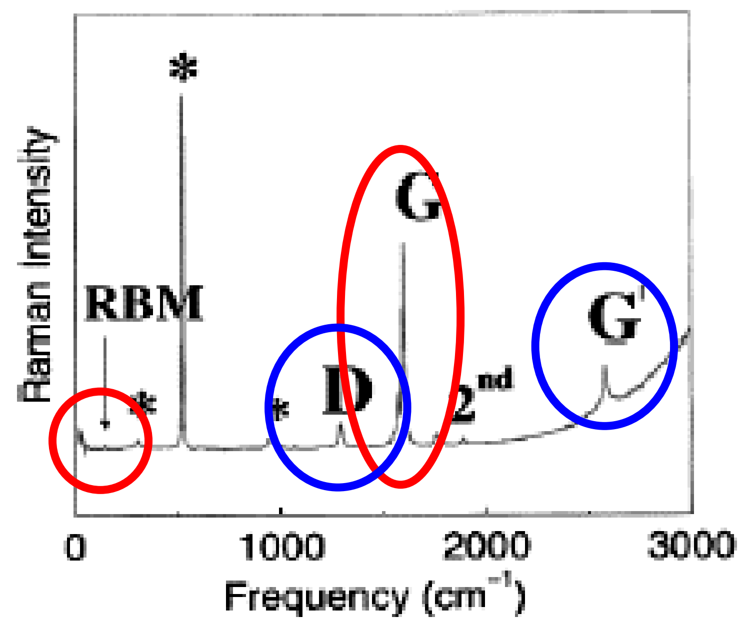
1D material:
- Normally week Raman signal strong due to resonance with vHS

→gives information about JDOS

Tight Binding Kataura Plot




CNT Raman modes:
- RBM-proportional to 1/D
- G-mode Tangential shear mode
- D- Defect mode near K point
- G'-mode: Doubly resonant mode near K-point




Note: RBM=A/dia +B
A, B vary depending on environment

# What do we learn from single SWNT measurements?

REPs:

- Precise measurement of system resonance, $E_{ii}$
- Resonance window
- Intermediate state lifetime broadening, $\sim\Gamma$

Area maps (micro-Raman)

- Physical extent of Raman active modes

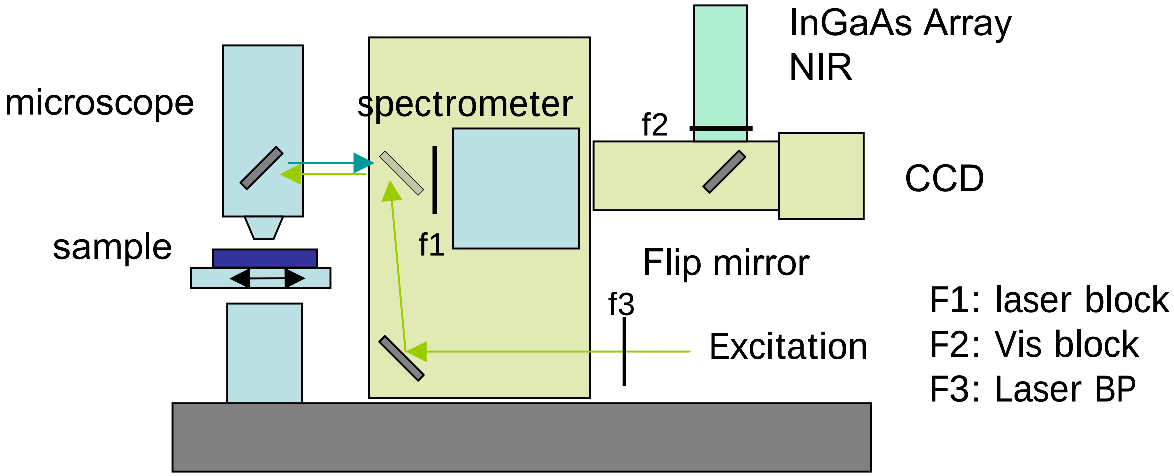
# Experimental system
# Samples
# Results

# Nanotube people

- Yan Yin
- Andy Walsh
- Nick Vamivakas
- Wolfgang Bacsa
- Bennett Goldberg
- Selim Ünlü

- Steve Cronin, Harvard
- Sasha Stolyarov, Harvard

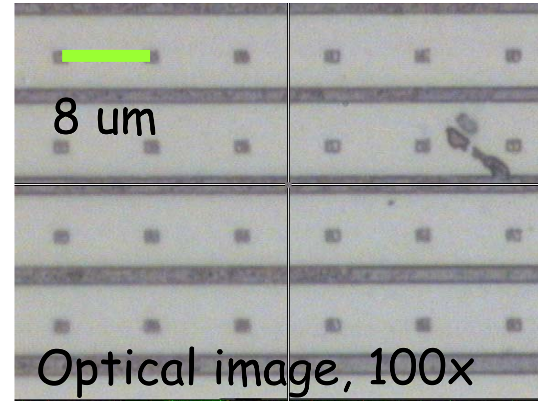
# Resonance Mapping Optical system




Limited range filter tunability by rotating F1 &F3

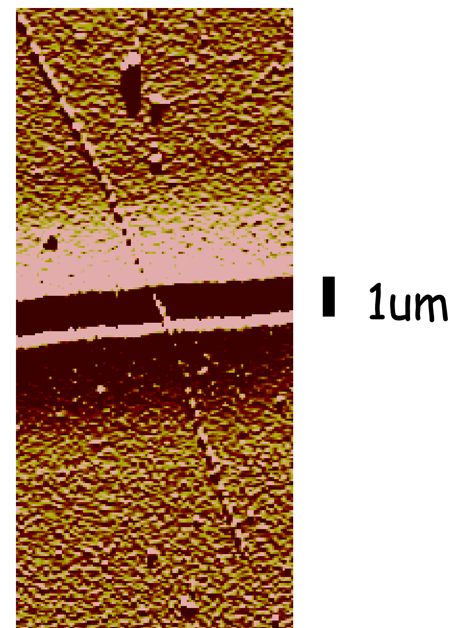
| | | | |
|---|---|---|---|
| Excitation: | | | |
| Individual lines | 488, 514, 532, and 633 nm | | |
| Tunable sources | Dye laser | 615-700 nm | 1.77-2.02 eV |
| | Ti-Saph laser | 700-850 nm | 1.46-1.77 eV |
| Detection: | Si CCD | Visible | 1.25-3.1 eV |
| | InGaAS | 0.9-1.6um | 0.78-1.38 eV |

# Samples




- Quartz substrates (no PL) with etched trenches, 1-1.5 um wide, ~0.3-0.5 um deep
- CVD grown tubes using methane gas at 900° C using a 1nm thick film of Fe deposited at RT

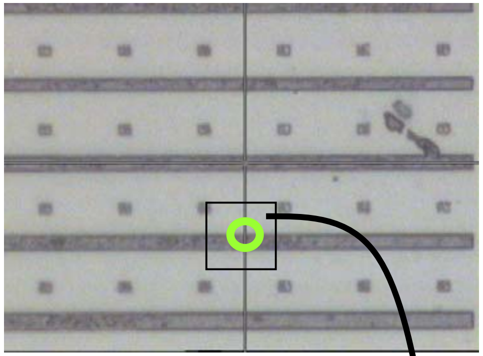
Trenches and markers make it possible to repeatedly return to the same tube

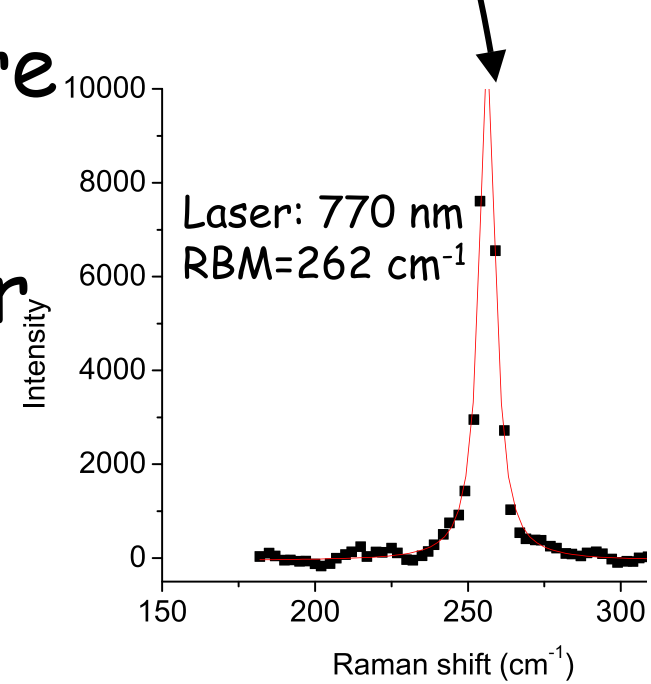



AFM image

# Finding tube w. Resonant Raman

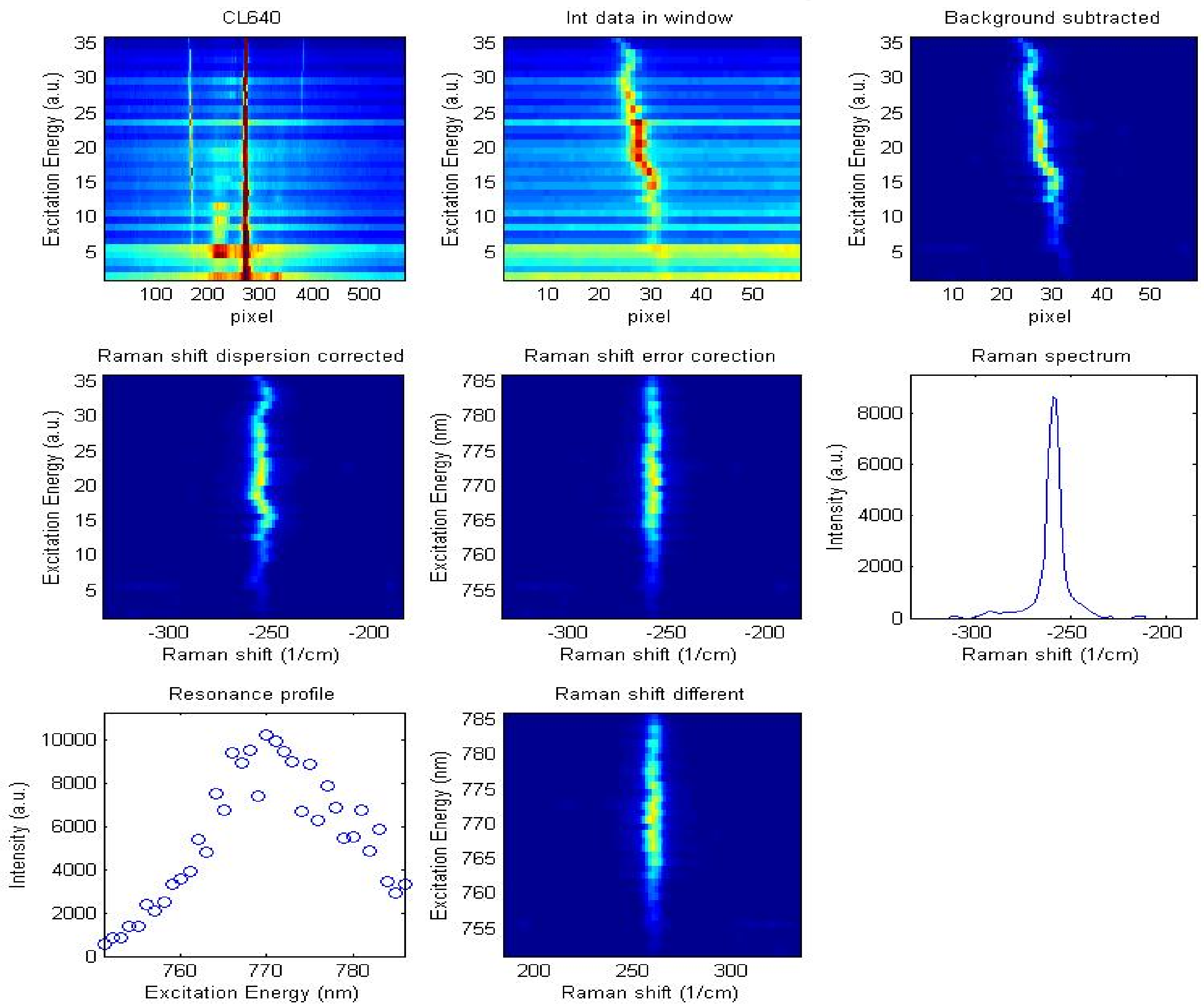
1. Find the tube using RBM mode
2. Excitation map: Tune the laser energy and measure spectra (PL, Raman)
3. Spatial map of tube over trench



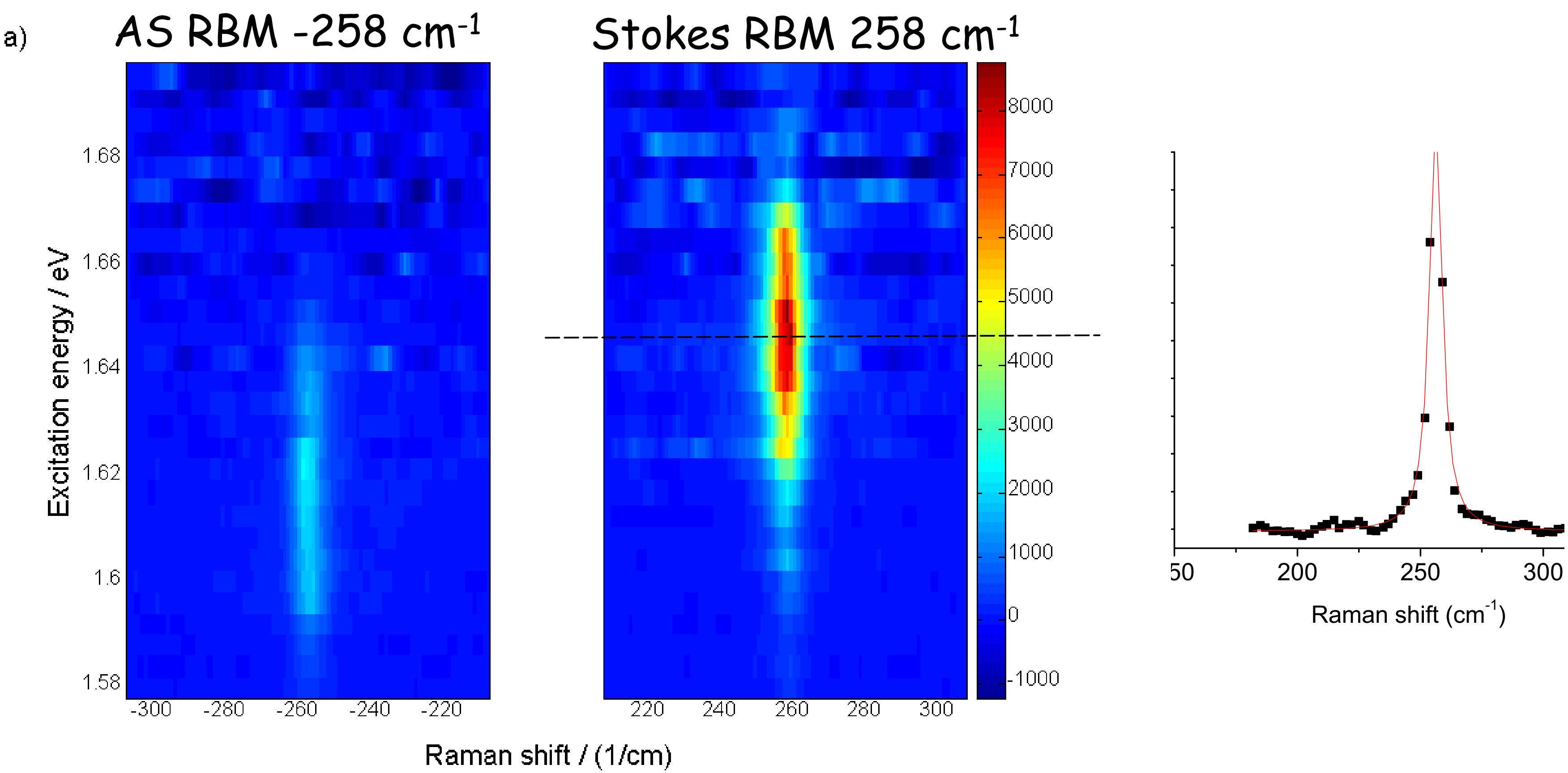



PL signal disappears quickly!

# Raman Intensity measurements, data handling



# Resonant Raman Excitation Maps




Stokes $I_{max}$ larger than AS $I_{max}$

Stokes and AS Intensity maximum do not coincide due to incoming and outgoing resonance

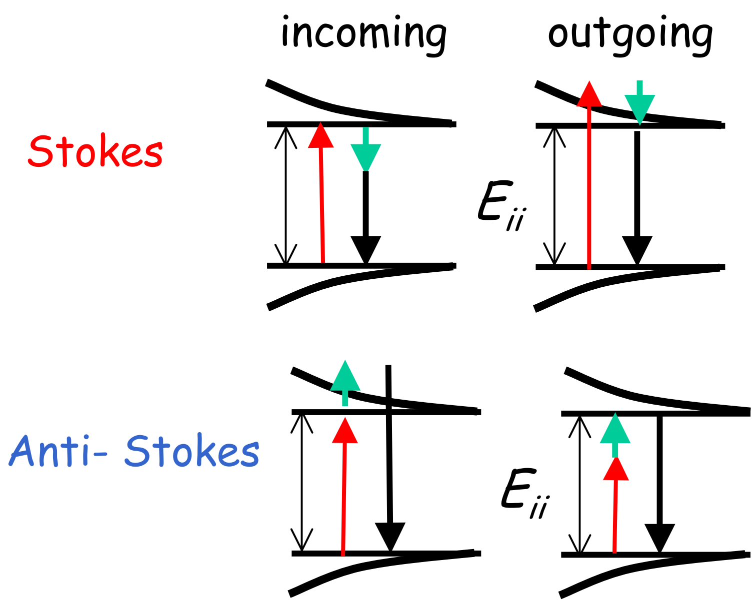
$$\frac{I_{AS}}{I_S} = I(E) \cdot e^{-\hbar\omega / kT}$$

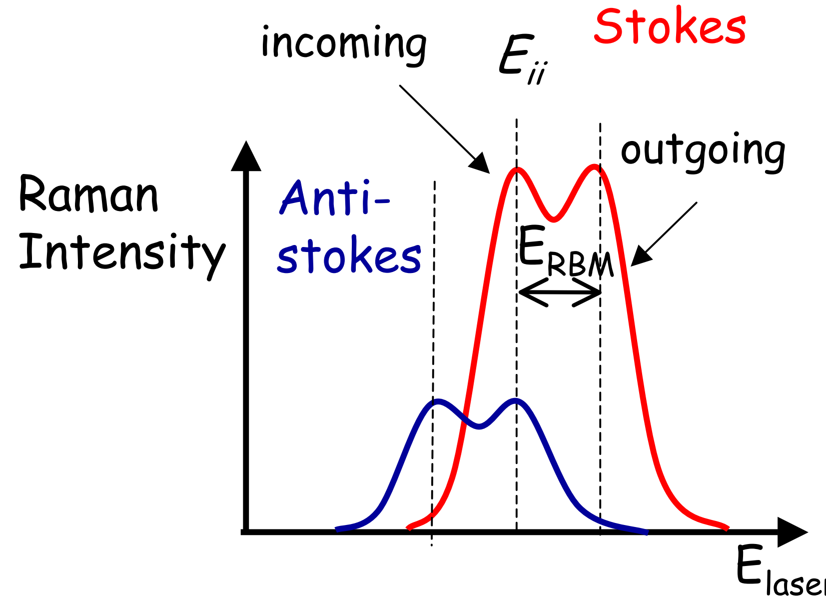
# Resonance Raman Intensity Profile; incoming and outgoing resonances

Raman intensity as a function of laser excitation energy

$$I \sim \left| A\sqrt{\frac{m^*}{2\hbar^2}}\left(\frac{L}{2\pi}\right)\int_{E_{ii}}^{E_{\max}} dE \, \frac{g(E)}{(E-\hbar\omega_L - i\eta)(E+\hbar\omega_Q-\hbar\omega_L-i\eta)}\right|^2$$

incoming outgoing




Resonance window $\sim E_{RBM} + \eta$

# Fitting Raman excitation profiles

Kramer Heisenberg time-dependent perturbation theory

$$I \sim \left| A\sqrt{\frac{m^*}{2\hbar^2}}\left(\frac{L}{2\pi}\right)\int_{E_{ii}}^{E_{\max}} dE \frac{g(E)}{(E-\hbar\omega_L - i\eta)(E+\hbar\omega_Q - \hbar\omega_L - i\eta)}\right|^2$$

DOS Band edge $$g(E) \sim (\sqrt{E_{ii}-E})^{-1}$$

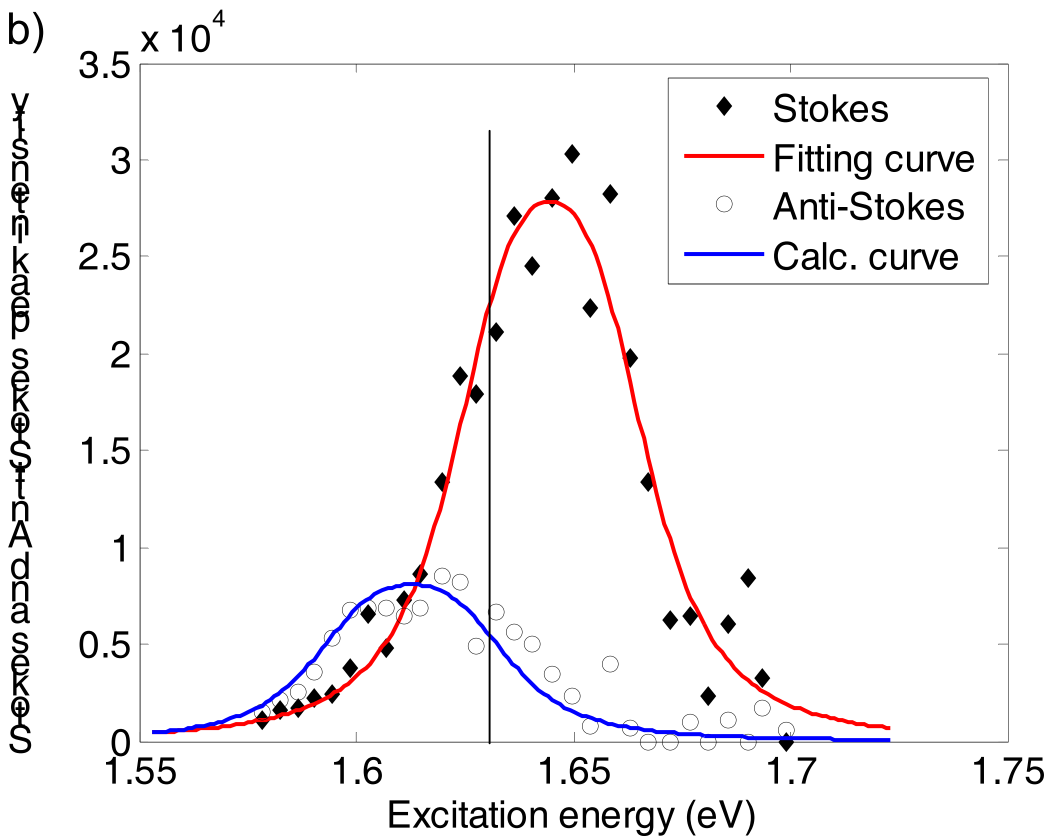
$$I(E_{laser}) = \delta \times A \times \left| \frac{1}{\sqrt{E_{laser}-E_{ii}-i\eta}} - \frac{1}{\sqrt{E_{laser} \mp E_{phonon} - E_{ii} - i\eta}} \right|^2$$

- Broadening from intermediate states, added
- Even with g(E) asymmetric, the resulting profile is symmetric.

→Asymmetry cannot be used to distinguish between single electron picture (asymmetric DOS) or exciton (symmetric DOS)

# Resonance Intensity profile

$$I(E_{laser}) = \delta \times A \times \left| \frac{1}{\sqrt{E_{laser} - E_{ii} - i\eta}} - \frac{1}{\sqrt{E_{laser} \mp E_{phonon} - E_{ii} - i\eta}} \right|^2$$




*$A$=1307±470,*
*$E_{ii}$=1.629 eV ±1.5meV,*
*$\eta$=17.8±3.5meV*
*RBM=258 cm$^{-1}$*

AS curve has no adjustable parameters

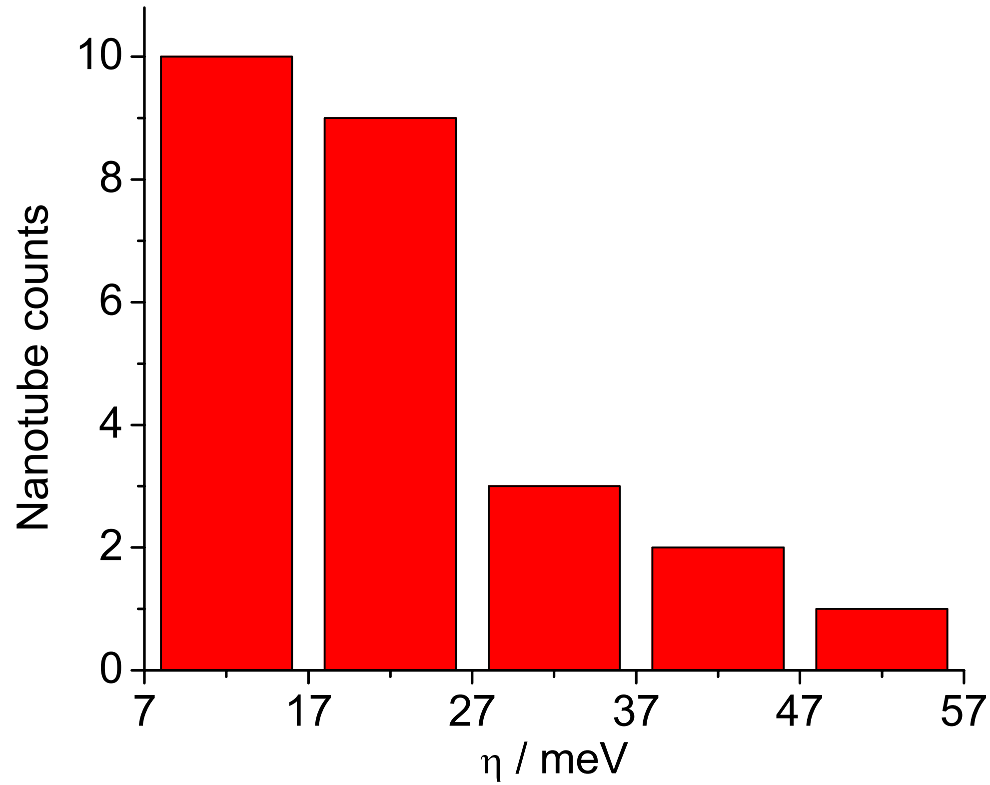
Good fit shows no heating takes place

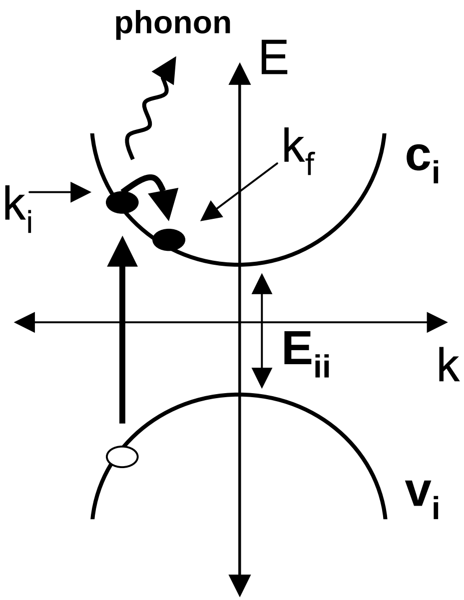
# REP's Broadening (23 tubes)

- Asymmetric broadening distribution

⇨ Possible that narrower REP's are due to intrinsic broadening, while some tubes are inhomogeneoulsy broadened

Broadening distribution (23 tubes)






# Lifetimes

## Electronic Relaxation By Electron-Phonon Scattering

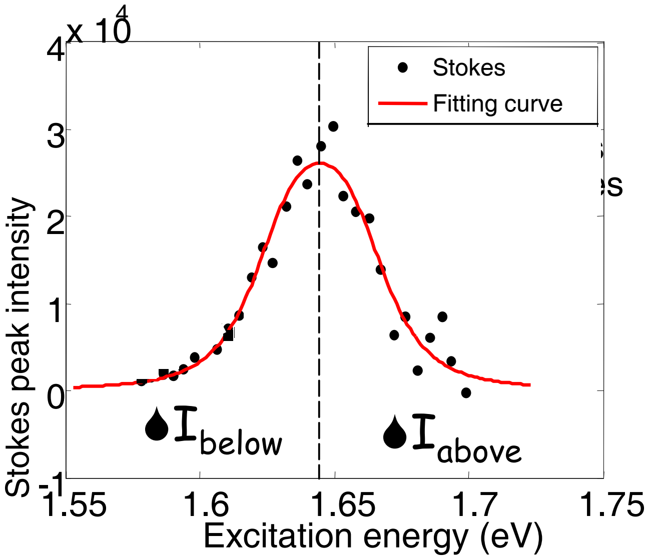
Calculate Probability per Unit Time of Transition by Fermi's Golden Rule for Electronic Transition by Phonon Emission

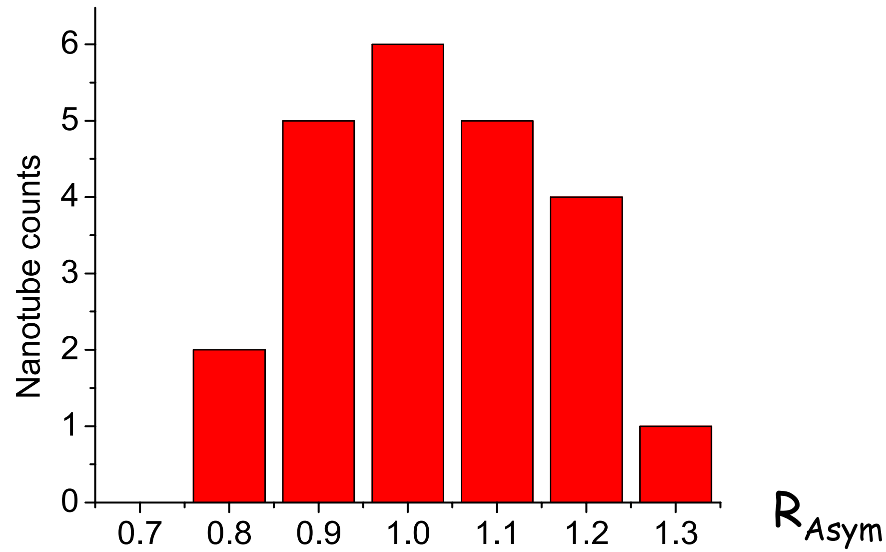
$$W_{k_i}^{ph} = \sum_{k_f} \frac{\left| \left\langle \Psi_{k_f} \middle| H_{e-ph} \middle| \Psi_{k_i} \right\rangle \right|^2}{\omega_{ph}(k_f - k_i)} \rho(E(k_f)) \times \delta\left(\omega_e(k_f) - \omega_e(k_i) - \omega_{ph}(k_f - k_i)\right)$$

Calculated transition rates ~0.02-0.1 ps
($\eta$~3-15 meV)
But:
Fermi's golden rule cannot be applied in our Raman case

PRB **71**, 045417 2005 J. Jiang *et al.*

# Peak Assymetry (23 tubes)

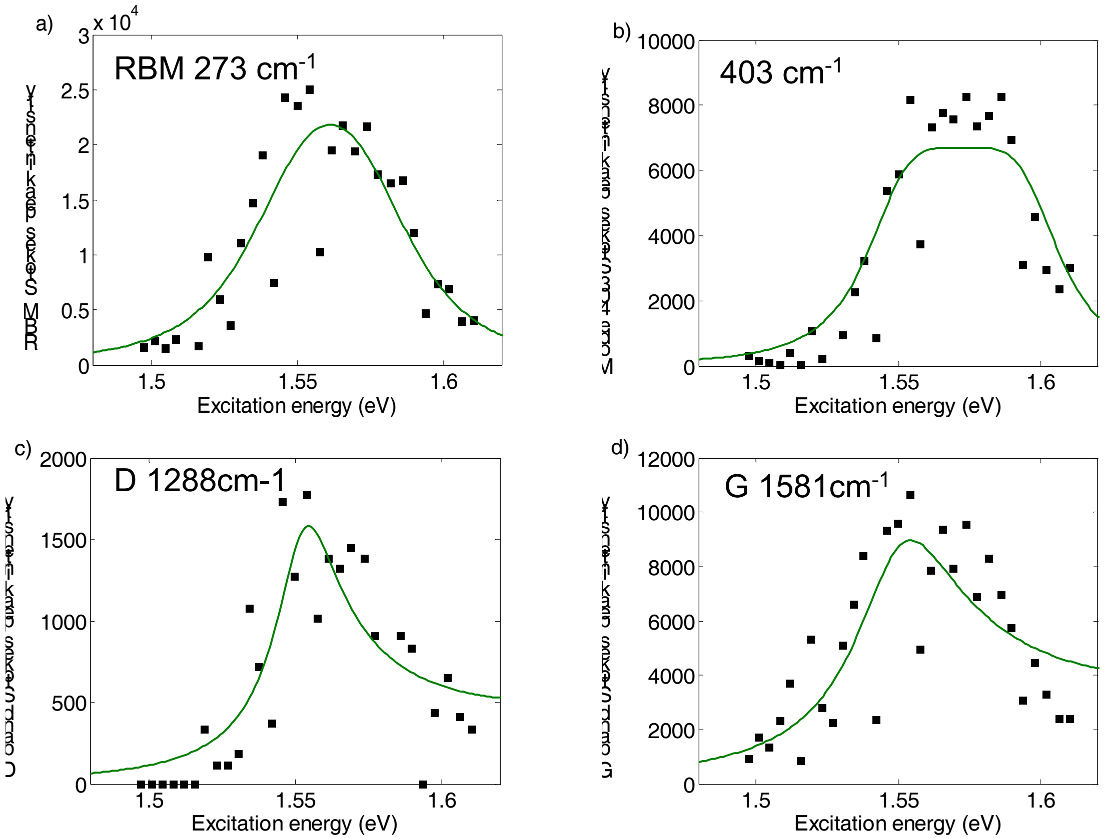


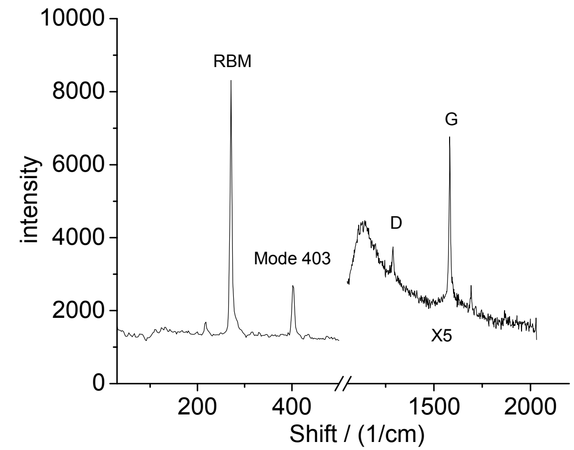




$R_{Asym}=\delta I_{above}/\delta I_{below}$

Within signal to noise, this distribution seems nearly symmetric
Possible cause of asymmetry : different broadening for incoming and outgoing resonances

# 4 REP's for one tube

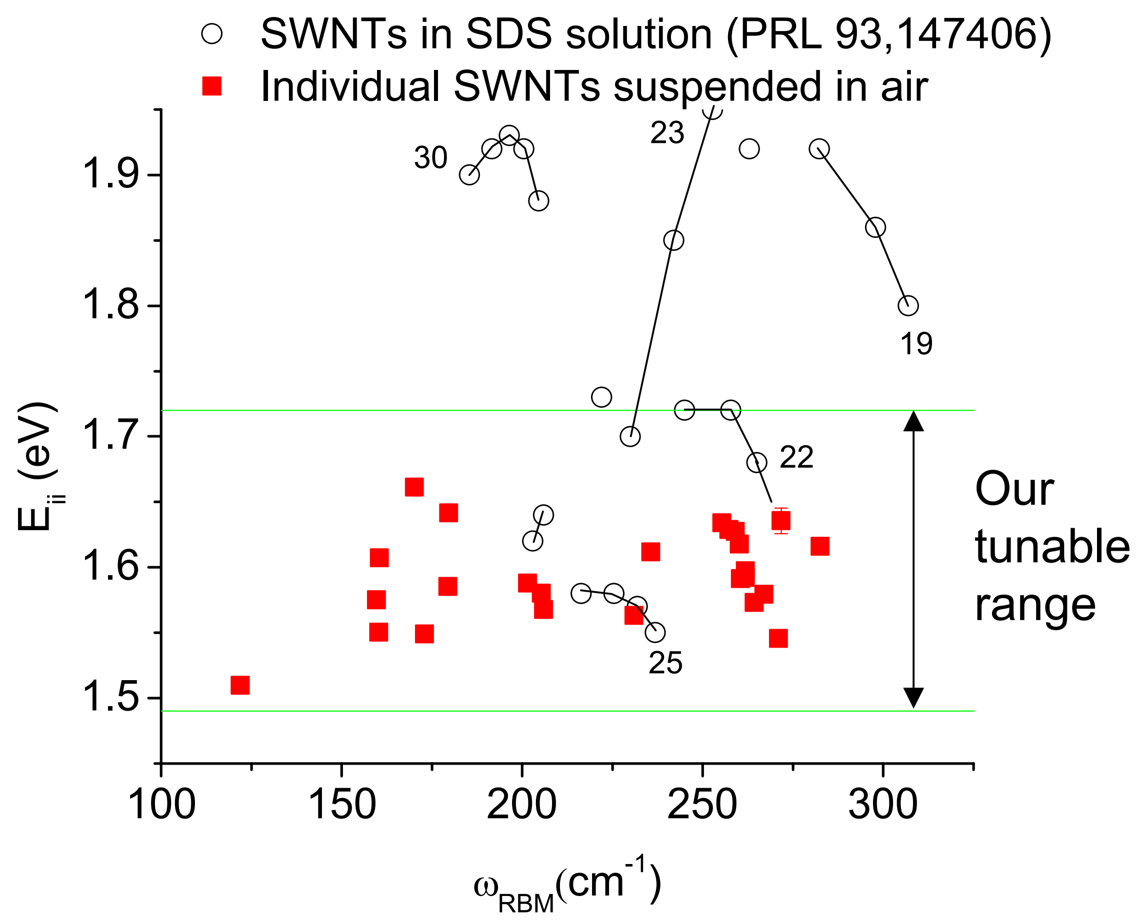



RBM: $E_{22}$= 1.545⊕3 meV $\eta$=28±8 meV
403: $E_{22}$= 1.548⊕4 meV $\eta$=18±10 meV
D: $E_{22}$= 1.552⊕3 meV $\eta$=11±4 meV
G: $E_{22}$= 1.549⊕5 meV $\eta$=18±6 meV

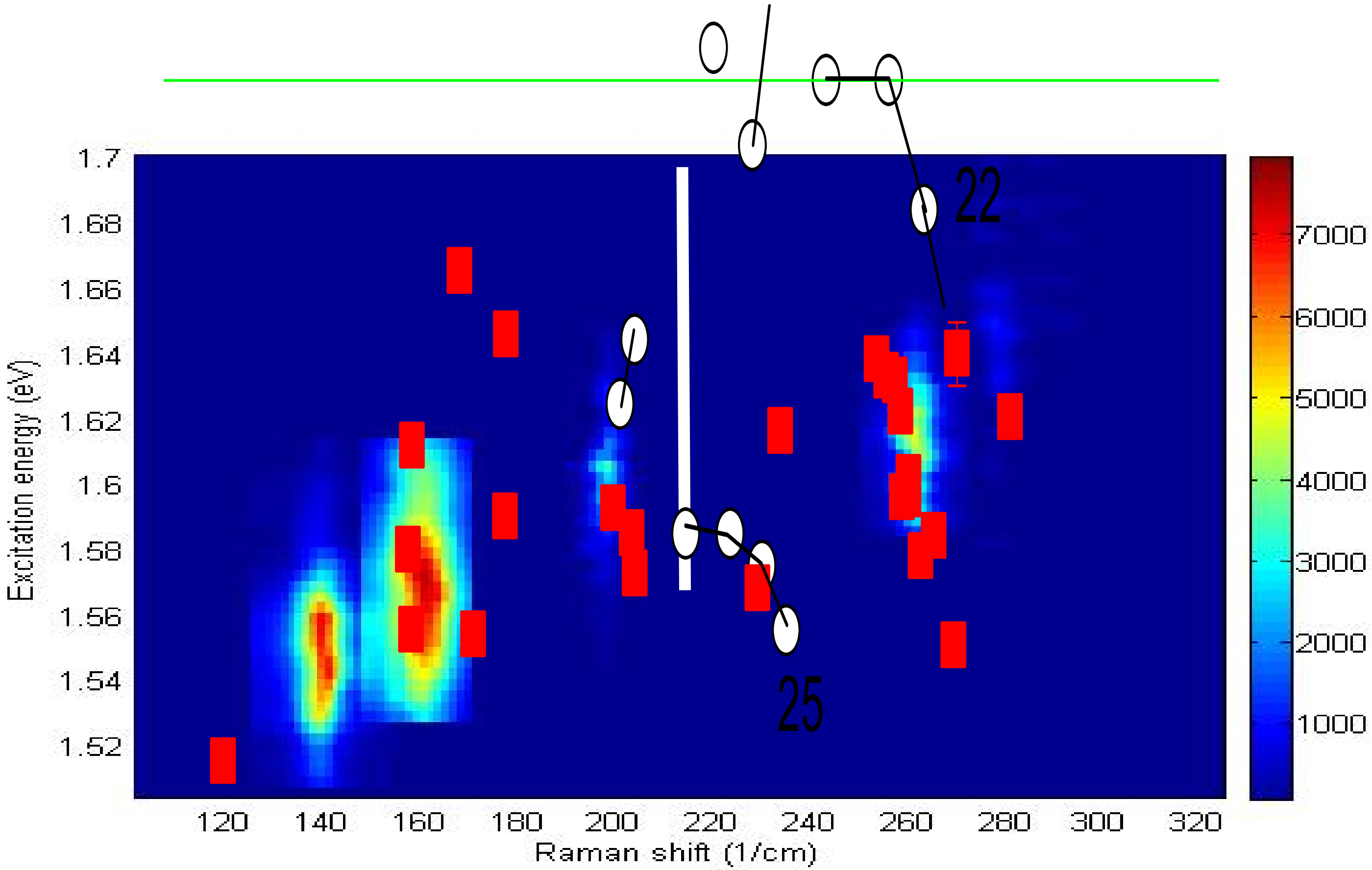
Note: For these measurements, $I_{RBM} > I_G$

# Map of all 23 tubes




NIST-NASA workshop Jan 2005

# Partial composite Resonance Raman Map




- Note: Resonance below center (incoming and outgoing resonance)

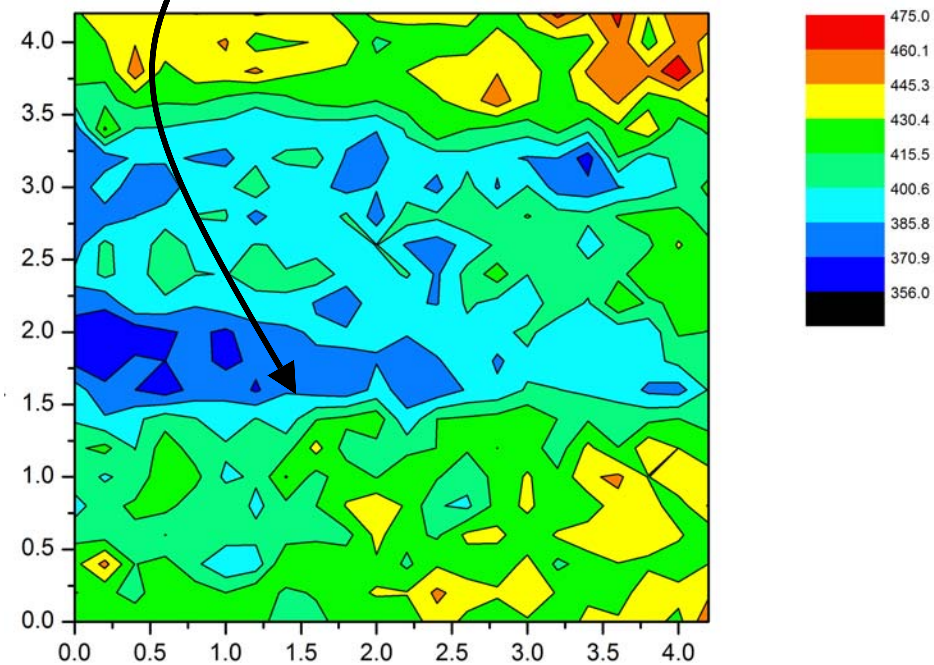
# Resonant Raman Profile Summary

- Resonant window depends on tube radius
  - Larger tube, smaller RBM, smaller window
- Resonance Profiles symmetric –but no discrimination between single electron-exciton models
- Single tube measurements of intrinsic linewidths (?)
- Both $E_{ii}$ and RBM have significant scatter for same (n,m) tubes -ensemble measurements inhomogeneously broadened
- Tubes in air has different (lower) resonance energy than tubes in SDS

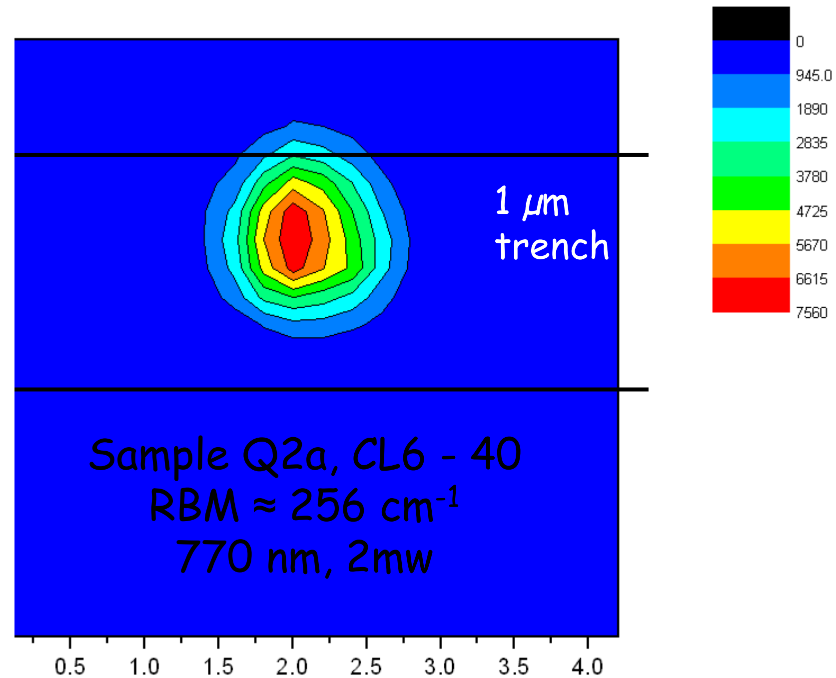
  $\rightarrow$ Exciton? Lower $\varepsilon$, higher $E_{b,}$ lower energy

# Spatial Raman mapping of suspended tube

Elastic laser light map
(maps out trench)

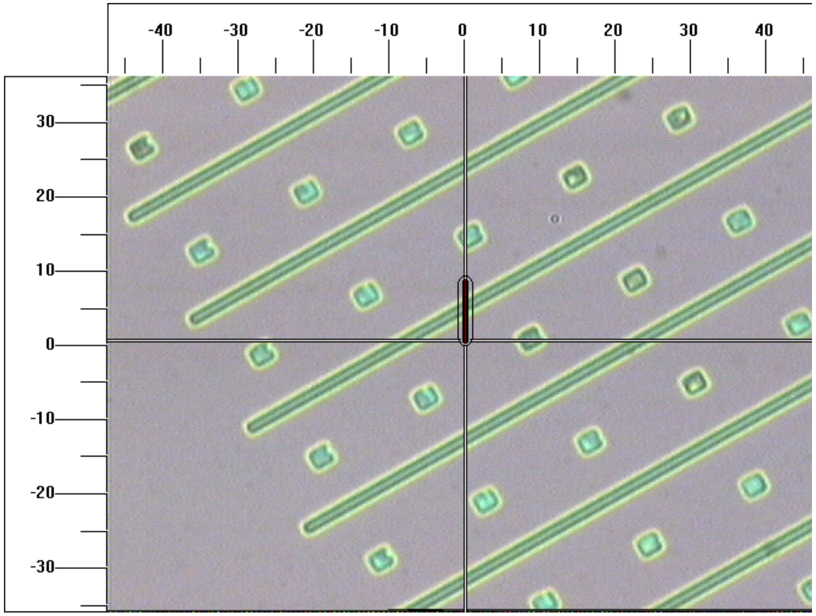


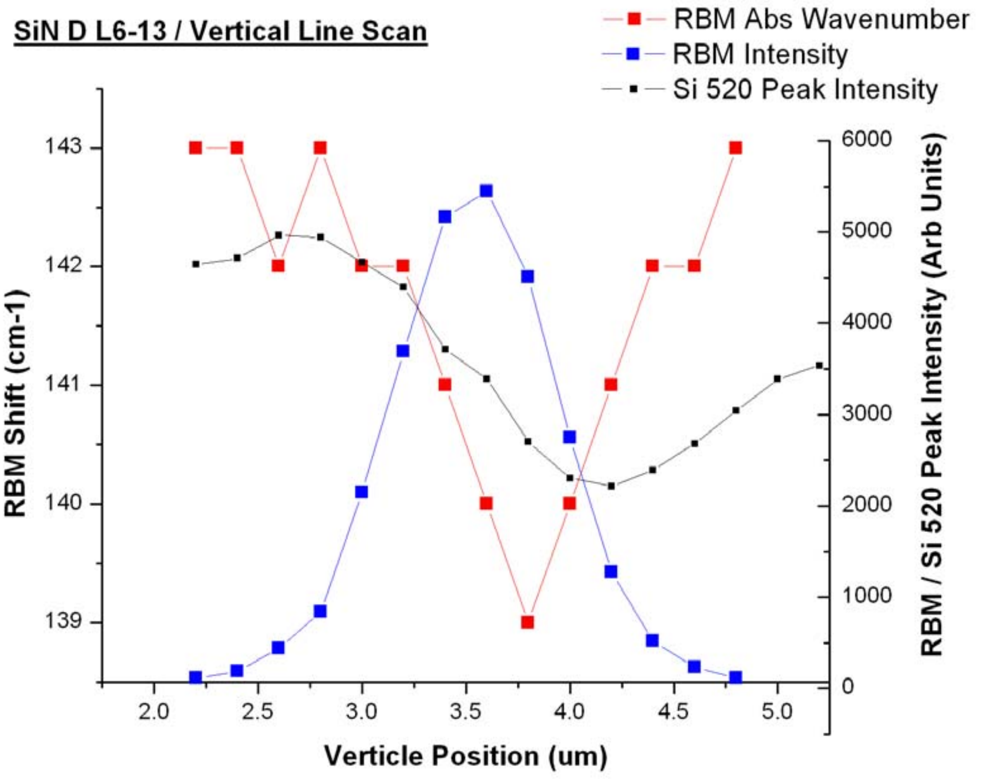

Raman map of RBM




Signal is (at least) 5-10 times stronger over trench

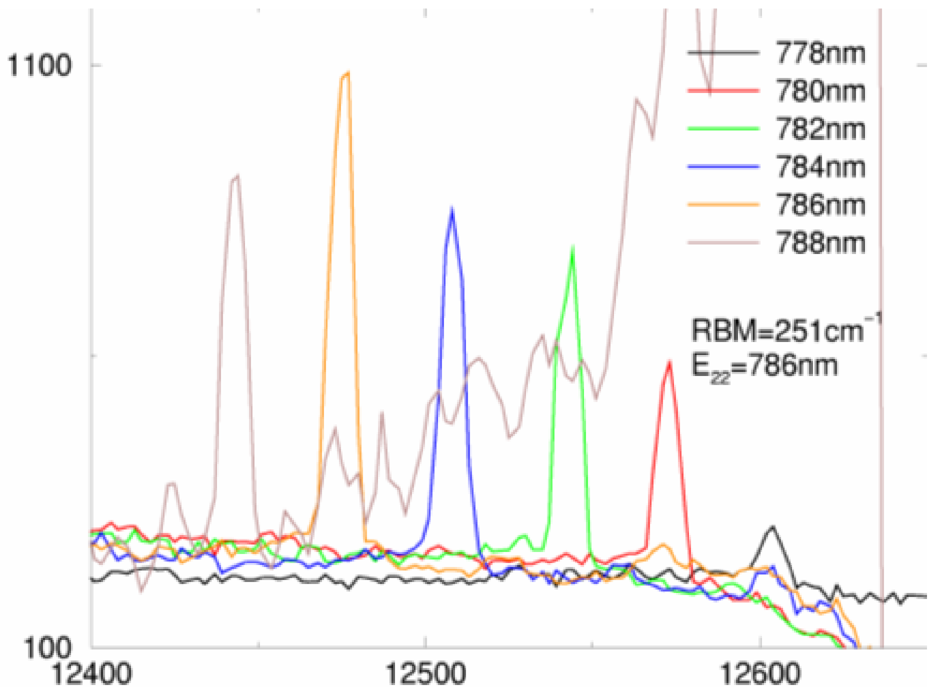
# Variation in RBM frequency (SiN substrate)



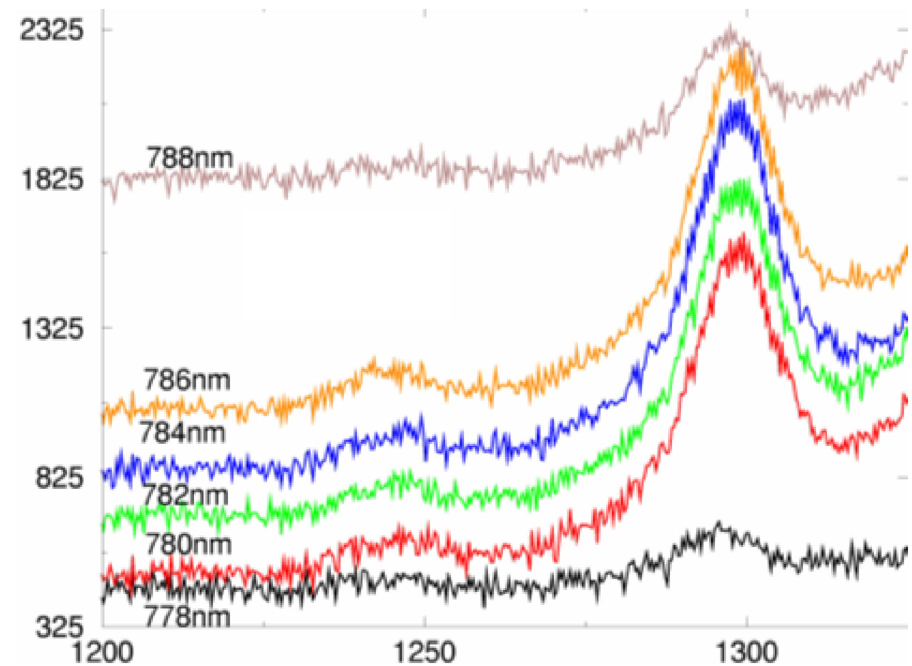



# Simultaneous PL and Raman from single nanotube

Raman Spectra




PL Spectra



# Summary

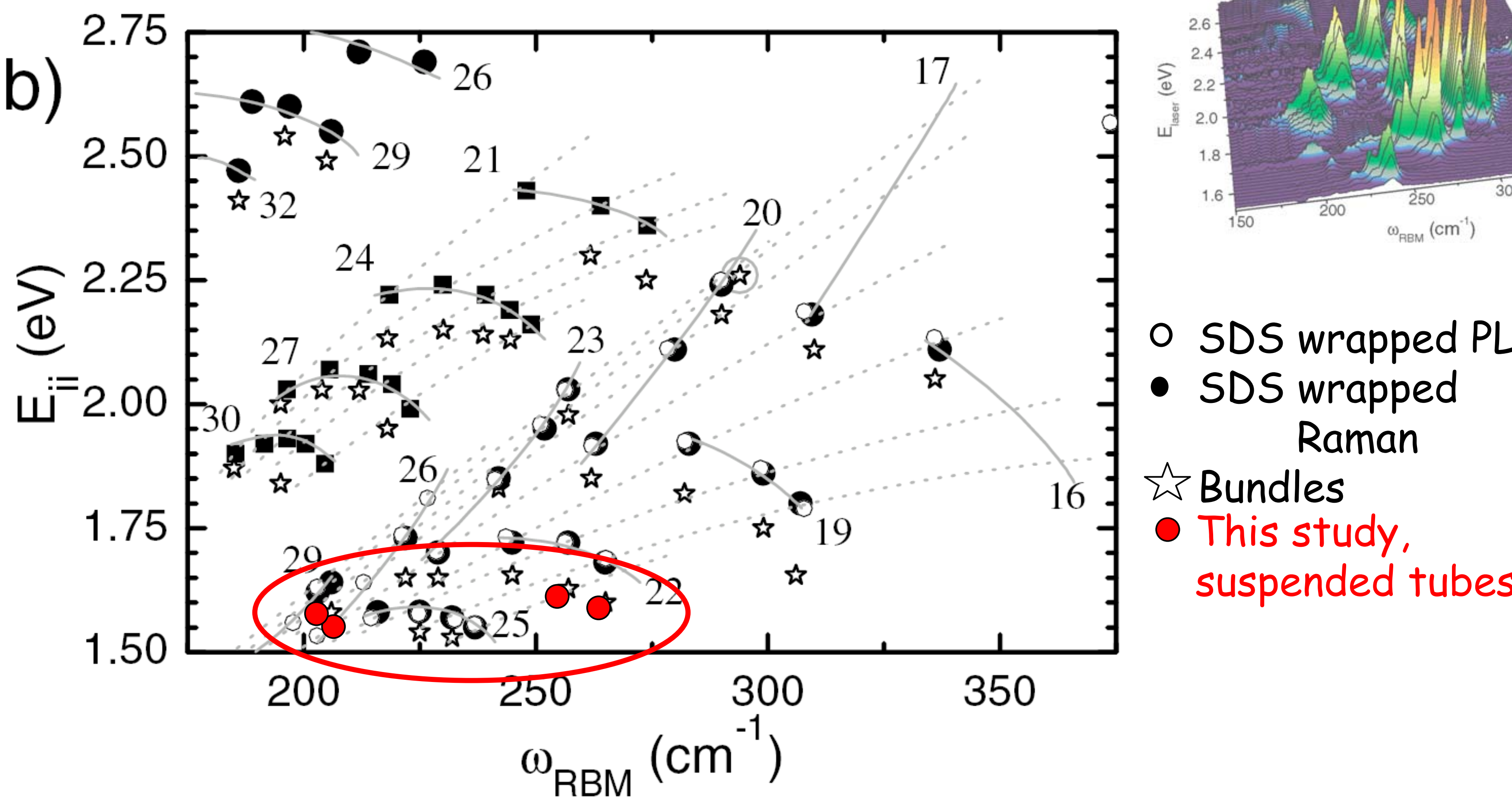
- PL transient, Raman signal persisting
- Raman signal strongest across trench (Compare PL)
- Large changes in RBM across trench (SiN)
- Large $E_{ii}$ shifts compared to tubes in SDS
- Considerable variation in RBM, $E_{ii}$ for given (n,m) tube

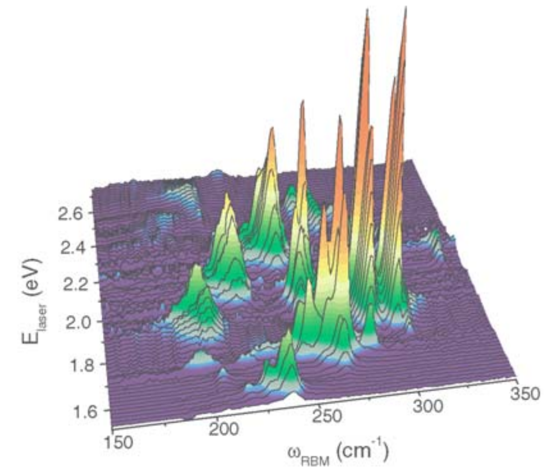
# Acknowledgments


- Many thanks to Mille Dresselhaus & her group
- Partial Funding From NSF NIRT and Boston University SPRInG grant

# Extensive Raman Map: SDS Ensemble

Fantini, PRL 93 (2004)

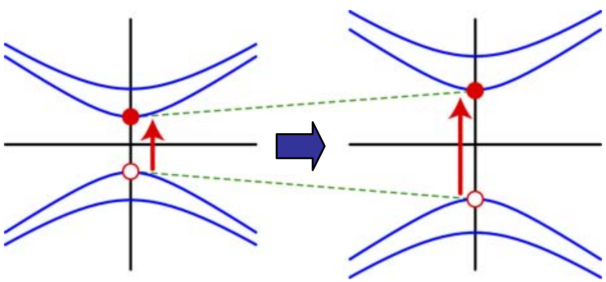


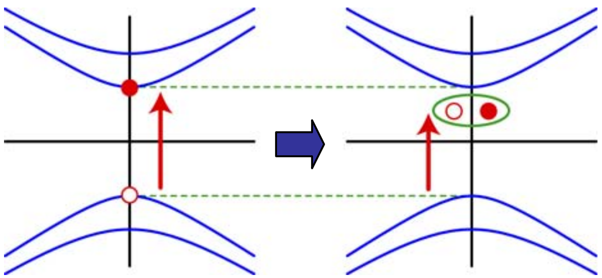



# Electron Interactions

One Particle Effects:
Exchange interaction renormalizes single particle energy levels
Increases observed energy gaps

Two Particle Effects:
Exciton:
Particle-Hole bound state
Decreases observed energy gaps





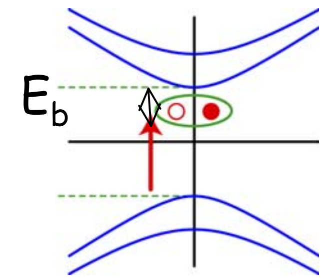
very large exciton binding energies predicted:
~ 0.3-1 eV but are nearly canceled by bandgap renormalization          C. Kane BU 2004

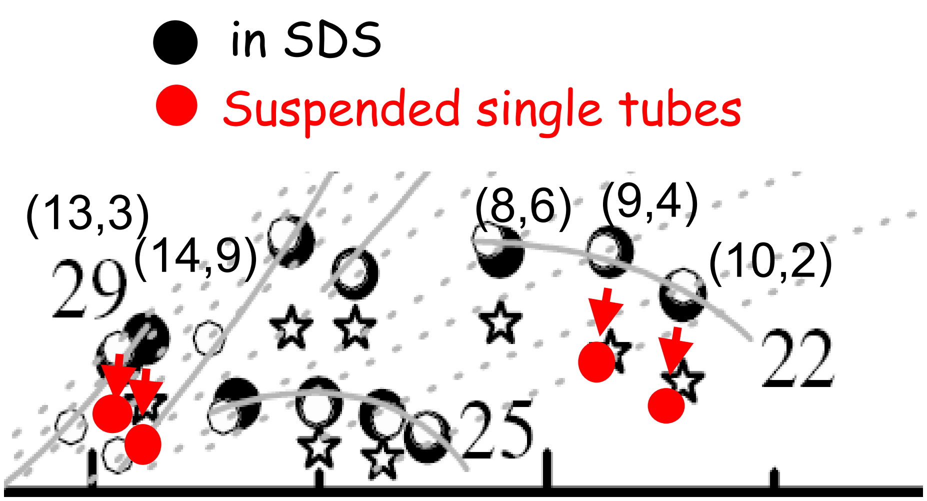
T. Ando, J. Phys. Soc. Japan (97)
C. Kane & Melee PRL **92** (2004)
C. D. Spataru, et al, PRL **92**, (2004)

$$E_b \sim (2/(2-\alpha))^2 \frac{\mu E_H}{\varepsilon^2 m_e}$$

# E-Shift due to change in exciton binding energy?

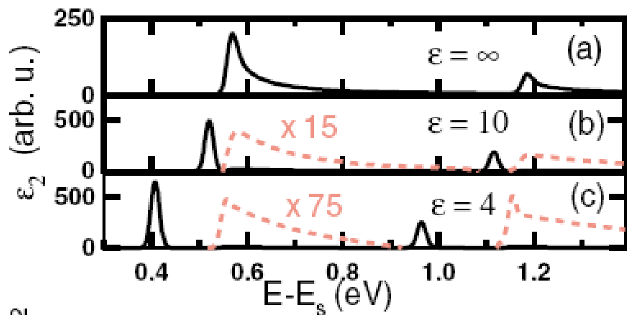
Exciton binding energy increases as dielectric constant decreases
$\rightarrow$ Lowers the optical excitation energy




$$E_b \approx A_b R^{\alpha-2} m^{\alpha-1} \epsilon^{-\alpha}$$

$\alpha$=1.4




C. D. Spataru, Tersoff, Avouris
PRL **92**, (2004)